Deposition of Functional Membranes by Through-Substrate Plane-Plate Dielectric-Barrier Discharge

H. Kobayashi[1], H. Kakiuchi[2], K. Yasutake[2], T. Suzuki[3], M. Noborisaka[3], and N. Negishi[1]

[1]Central Research Laboratory, Hitachi, Ltd., 1-280 Higashi-koigakubo Kokubunji-shi, Tokyo, 185-8601 Japan

[2]Department of Precision Science and Technology, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka Suita, Osaka, 565-0871, Japan

[3]Center for Science of Environment, Resource and Energy, Keio University, 3-14-1 Hiyoshi Kohoku-ku, Yokohama, 223-8522, Japan

E-mail: hiroyuki.kobayashi.sy@hitachi.com

Abstract. A novel roll-to-roll deposition method, namely, "through-substrate plane-plate dielectric-barrier discharge," was developed. This method uses a dielectric-barrier-discharge plasma plate, which has antenna and ground lines in a dielectric material, as an electrode. A film substrate was placed on the electrode so that an electric field, which passes through the substrate, generates a plasma above surface of the substrate. This method can avoid unexpected deposition on the electrode, which causes dust-particle contamination. In a preliminary experiment, deposition rates of Si, SiN, and Diamond-Like-Carbon were about 1, 1.5 and 5 μm/min, respectively. When there was a space between the plasma plate and the substrate film, plasma was generated on the back side of the substrate film, and then the deposition on the surface of the substrate film was prevented. This back-side discharge was suppressed by supplying nitrogen gas to the back-side of the substrate film.

1. Introduction

Low-cost mass-production of gas barrier films is required for fabrication of flexible devises such as electronic papers, photovoltaic (PV) and organic light-emitting diode (OLED) devises. Atmospheric plasma has been widely studied for its use in fabrication of gas barrier films due to its high deposition rate of a few micrometers per minute [1-5]. As an atmospheric-plasma source, dielectric-barrier discharge (DBD) [6-13], inductively coupled plasma (ICP) discharge [14], DC arc discharge [15], and microwave-excited plasma discharge [16] have been developed. The DBD plasma has been widely studied for a large-scale atmospheric plasma by parallel-plate configuration. However, when it is used for the deposition processes, several issues should be solved. For example, formation of unexpected deposition on the electrode should be suppressed because the deposition layer, which peels off the electrode, causes dust-particle contamination. In addition, a process gas should be uniformly fed in a large-size plasma to increase uniformity of deposition layers on the films. Moreover, low-temperature processes are required from the viewpoint of less heat resistance of substrate films such as polyethylene-terephthalate (PET) film. Thus, many types of new DBD plasma technique have been proposed. A plane-plate DBD plasma source that antenna and ground lines are formed in a dielectric material has been used in a plasma display panel and generates large-scale plasma [10-12].

In the present study, a novel roll-to-roll deposition method, namely, "through-substrate plane-plate dielectric-barrier discharge" was developed by using the DBD plasma plate. This method eludes unexpected deposition on the electrode.

2. Experimental

A schematic view of the through-substrate plane-plate dielectric-barrier discharge method is shown in Fig. 1, and the plane-plate DBD plasma source (DBD plasma plate) is shown in Fig. 2. As for the plasma plate, a plurality of antenna lines and ground lines were placed alternatively on a dielectric substrate plate and covered with a dielectric layer. Plasma is generated at the surface of the dielectric layer above the gap between the antenna and ground lines. A substrate film is placed on the surface of the plasma plate so that the substrate film is considered as a part of the dielectric layer of the plasma plate. Electric field, which passes through the substrate film, generates plasma above the surface of the substrate film. The plasma does not touch the plasma plate, so an unexpected deposition layer does not form on the plasma plate. The antenna and ground lines are placed on the back side of the substrate film, thus an optimal gas supply system can be freely designed in the region above the substrate film to improve the uniformity of the deposition layer.

The width of a gap between the antenna and ground lines (D in Fig. 2) was 1 mm. The thickness of the dielectric layer (T in Fig. 1) was 0.05 mm. The widths of the antenna and ground lines (W in Fig. 2) were 0.2 or 1 mm. The lengths of the antenna and ground lines (L in Fig. 2) were 100 mm. Alumina was used for the substrate plate and the dielectric layer of the plasma plate. A 0.05-mm-thick PET film was used as the substrate film.

The experimental setup is shown schematically in Fig. 3. The plasma plate was set in a chamber. A DC power-supply was connected to an inverter circuit, which generated a high-frequency discharge

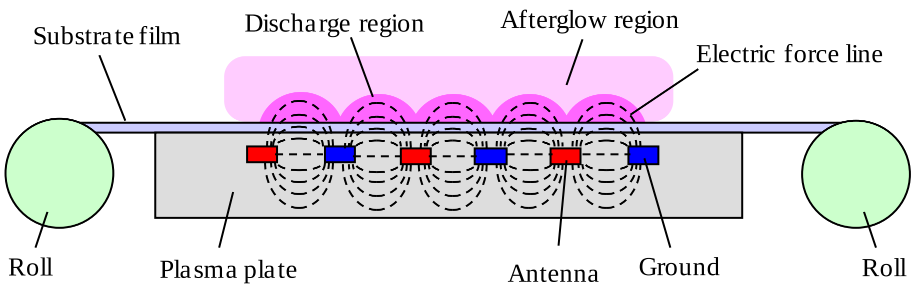

Fig. 1 Schematic view of a roll-to-roll deposition method by through-substrate plane-plate dielectric-barrier discharge.

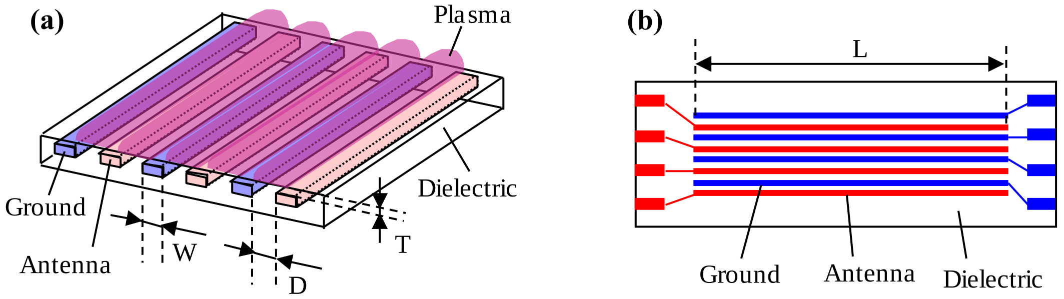

Fig. 2 Schematic view of dielectric-barrier-discharge plasma-plate. (a)Cross section view, (b)Top view of electrode pattern.

power of about 20 kHz and 0-2 kV (Hereafter, discharge voltage denotes half value of the peak-to-peak voltage.) The electric power consumed by plasma discharge was about 75% of that supplied to the inverter circuit. A PET film was fixed on the plasma plate or wound by a roll set in the chamber. He/SiH_4, He/SiH_4/NH_3/H_2, and Ar/C_2H_2 were used as the process gases for deposition of Si, SiN, and Diamond-Like-Carbon (DLC) layers, respectively. The chamber was connected to a vacuum pump via a valve. The process pressure was maintained at 1 atm by changing the opening degree of the valve.

3. Results and discussion

Photographs of during and after deposition are shown in Figs. 4(a) and (b), respectively. A PET film was fixed on the plasma plate by a polyimide tape, as shown in Fig. 4(c). Width of both the antenna and ground lines was 0.2 mm. He/SiH_4 was supplied as the process gas with SiH_4 mixture ratio of 0.1%. The flow rate of the process gas was 10 L/min. The discharge voltage was 1.3 kV. Discharge power supplied to the plasma was only about 0.1 W/cm^2, so the plasma light was weak. A little bright plasma-light was locally observed, for example, at position Z in Fig. 4(a). At that position, plasma was generated on the back side of the PET film because there was a discharge space between the film and the plasma plate. At position Z, the deposition-layer was thin as shown as Z' in Fig. 4(b). It is clear that suppressing the back-side discharge is important for improving uniformity of the deposition-layer thickness.

The measured deposition rates of Si, SiN, and DLC layers (averaged across the plasma plate) are plotted in Figs. 5(a) and (b). The width of the antenna and ground lines (W) was 0.2 mm for a Si layer deposition. The discharge voltages were 1.3 and 1.5 kV, respectively, for SiH_4 mixture ratios of 0.1 and 0.3%. Discharge powers consumed by plasma were 0.1 and 0.13 W/cm^2 for SiH_4 mixture ratios of

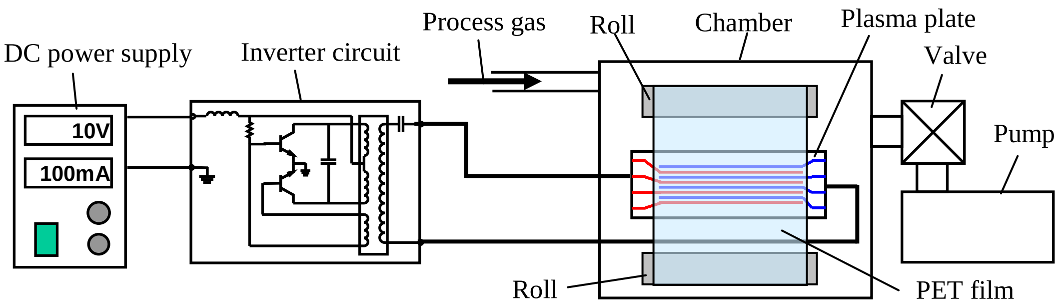

Fig. 3 Schematic view of experimental setup.

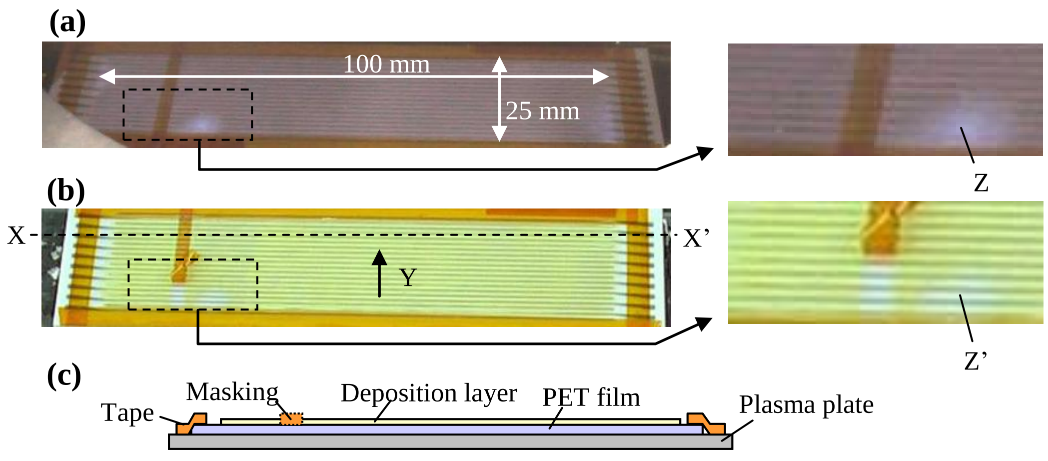

Fig. 4 Example of during plasma discharge and deposition results. (a) During deposition process, (b) After deposition process, (c) Schematic view of the sample for cross section of X-X' in (b).

0.1 and 0.3%, respectively. For a SiN layer deposition, W of the plasma plate was 1 mm. Mixture ratios of SiH_4, NH_3, and H_2 were 0.1, 1, and 1%, respectively. The discharge voltage was 1.4 kV and a discharge power consumed by plasma was about 0.3 W/cm^2. Flow rate of the processes gas was 10 L/min and process pressures were 1 atm for both Si and SiN deposition. For DLC layer deposition, W of the plasma plate was 1 mm. The discharge voltage was 1.5 kV and discharge power was about 0.7 W/cm^2. Flow rate of the process gas was 3 L/min, and process pressure was 1 atm. Deposition rates were 1 and 1.5 μm/min for Si and SiN at SiH_4 mixture ratio of 0.3% and 0.1%, respectively. Deposition rate of DLC increased with increasing C_2H_2 mixture ratio, reaching about 5 μm/min at C_2H_2 mixture ratio of 3%. The order of the magnitude of these deposition rates is the same as that attained with other atmospheric-plasma methods [1-5]. Thus, the present deposition method is useful for high deposition-rate processes.

Distribution of the deposition-layer thickness across the film measured by laser microscope is shown in Fig. 6. The direction of the scan is marked as Y in Fig. 4(b). SiH_4 mixture ratio was 0.3%. The process time was 5 min. Deposition rate was high above the antenna and ground lines (A in Fig. 5) and between the antenna and ground lines (C in Fig. 6). The thickness of the deposition layer at position B (between A and C), which was measured with a scanning electron microscope (SEM) was at least about 0.5 μm.

SEM images of the surface of the Si deposition layers are shown in Figs. 7(a), (b), and (c), which correspond to positions A, B, and C in Fig. 6, respectively. Many particles were buried in the deposition layer. The surface of the deposition layer shown in Fig. 7(c) was coarser than that in Figs. 7(a) and (b). Moreover, many particles that were not buried in the deposition layer were visible at position C.

The distribution of electric-force strength above the film is shown in Fig. 8. It was calculated by roughly assuming that the relative permittivities of the dielectric layer, the PET film, and the gas phase were 6, 3, and 1, respectively. The voltages of the antenna and ground lines were 1.3 and 0 kV, respectively. Positions A, B, and C in Fig. 8 correspond to positions A, B, and C in Fig 6. The electric

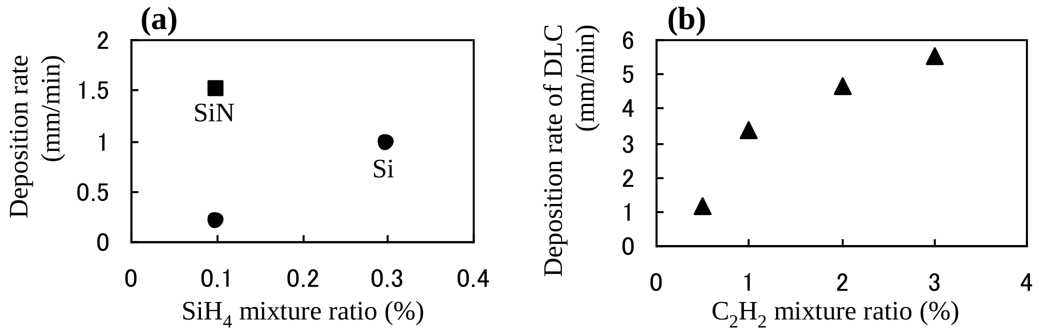

Fig. 5 Deposition rate of (a) Si and SiN, (b) DLC layer.

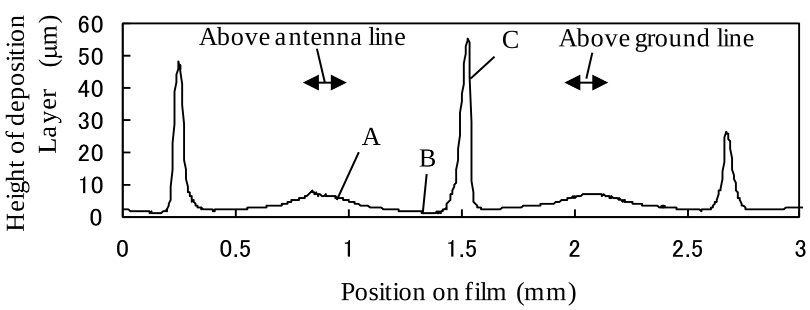

Fig. 6 Distribution of Si deposition layer thickness across the PET film.

force at position A is two-times stronger than that at position C. It is clear that the surface of the deposition layer became rough at the position, where electric field strength was low. This result indicates that the agglomeration reaction was faster than the decomposition reaction of precursors, where electric field was weak. In this experiment, the process gas was not intentionary supplied to the plasma to increase the gas flow velosity for the purpose of supressing particle formation in the plasma. A study on reducing particle formation by increasing gas flow in the plasma is left for future work.

Measures to avoid the back-side discharge are described as follows. Minimum voltage required for the discharge was measured under three conditions. The discharge gas was He at 1 atm. Figure 9(a) denotes that the dielectric layer thickness (T) was 0.05 mm and PET film was not placed on the plasma plate. The discharge voltage was 0.6 kV. It can be assumed that the condition shown in Fig. 9(a) is the same as the condition shown in Fig. 9(a'), which indicates that there was sufficient space at the back side of the PET film. Figure 9(b) shows that the discharge voltage was 0.7 kV when T of the

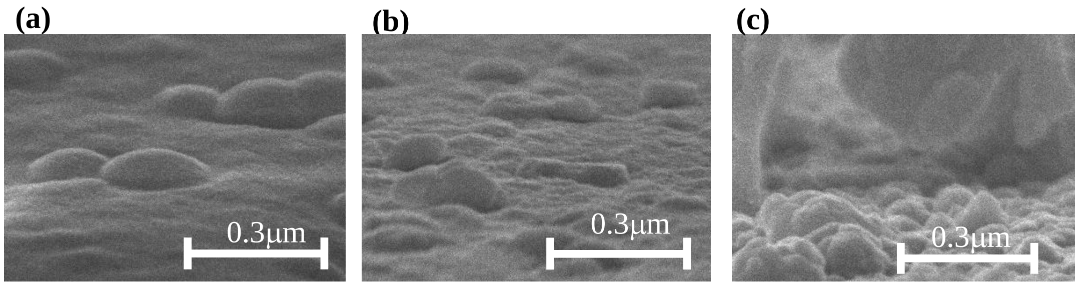

Fig. 7 SEM images of surface of Si deposition layer. Figs. (a), (b), and (c) correspond to A, B, and C in Fig. 6.

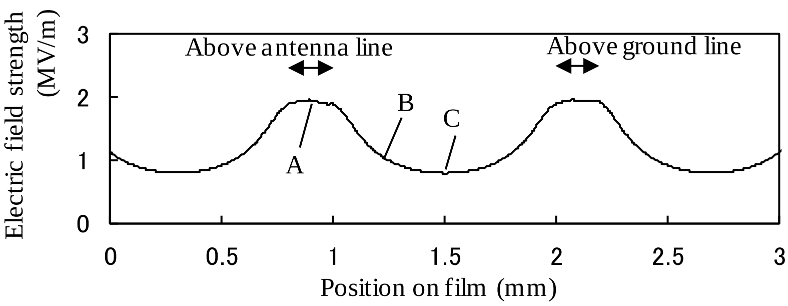

Fig. 8 Electric field strength above the film.

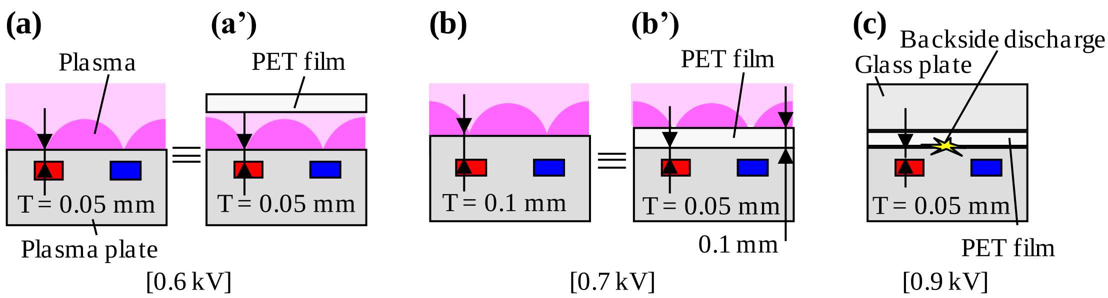

Fig. 9 Minimum discharge voltage of (a) 0.6 kV for T of 0.05 mm, (b) 0.7 kV for T of 0.1 mm, and (c) 0.9 kV for T of 0.05 mm with a PET film and a glass plate. (a) and (b) can be assumed to be equal to (a'); the PET film float above the plasma plate and (b'); about 0.1-mm-thick PET film was placed on the plasma plate for T of 0.05mm, respectively.

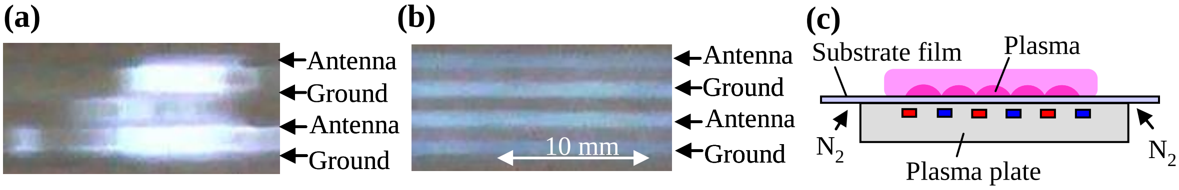

Fig. 10 (a) Photograph of back-side discharge, (b) Plasma on the surface of the PET film, (c) Schematic view of N_2 gas supply to the back side of the film.

plasma plate was 0.1 mm and no PET film was placed on the plasma plate. It can be roughly assumed that the condition shown in Fig. 9(b) is the same as the condition shown in Fig. 9(b'), which indicates that the dielectric layer thickness T was 0.05 mm for the relative permittivity of 6-10 (alumina) and about 0.1 mm-thick PET film for the relative permittivity of 3 was placed on the plasma plate. According to the comparison of Figs. 9(a') and (b'), plasma is generated at the back side of the substrate film rather than surface of the substrate film when the substrate film floats above the plasma plate. When T of the plasma plate was 0.05 mm and a glass plate was placed on the PET film to reduce the distance between the PET film and the plasma plate, as shown in Fig. 9(c), the voltage required for the back-side discharge was 0.9 kV. The comparison of Figs. 9(b') and (c) reveals that the back-side discharge can be prevented by reducing the space between the plasma plate and the substrate film.

There is another measure to suppress the back-side discharge. The discharge voltage of the process gas, which is sufficiently diluted by a rare gas, is lower than that of N_2 gas. About 0.5 and 2 kV were required for plasma discharge for He and N_2 at 1 atm, respectively, when T and D of the plasma plate were respectively 0.05 and 0.2 mm. This result indicates that discharge voltage required for N_2 is higher than that for He by a few times. A photograph of back-side discharge is shown in Fig. 10(a). The process gas was Ar/C_2H_2 (1%) at 1 atm. A bright light from the plasma was observed between the antenna and ground lines. On the contrary, N_2 gas was supplied near the region at the back side of the film by using another gas-supply line as shown in Fig 10(c), so that the N_2 gas was filled the gap between the PET film and the plasma plate in case that the PET film floated above the plasma plate. In this case, as shown in Fig. 10(b), the back-side discharge disappeared, and a weak plasma light was emitted from the region above the antenna and ground lines. This plasma-light emission indicates that the plasma was generated above the PET film. It is clear that the back-side discharge can be prevented by supplying N_2 gas to the back of the substrate film.

4. Summary

Deposition of Si, SiN and DLC layers by through-substrate plane-plate dielectric-barrier discharge was investigated. Deposition rates of the Si, SiN and DLC layers were about 1, 1.5 and 5 μm/min, respectively, which are the same order of the magnitude as those attained by other atmospheric-plasma methods. This method can avoid formation of an unexpected deposition layer on the plasma source, which causes dust-particle contamination. Deposition of particles formed in the plasma was observed because no intentional gas flow was generated in the plasma. In case that there is a space between the substrate film and the plasma plate, the plasma is generated on the back side of the substrate film, and the deposition on the surface of the substrate film is disturbed. The back-side discharge can be suppressed by reducing the space between the substrate film and the plasma plate. And also supplying N_2 gas to the back of the substrate film prevents the back-side discharge, when the process gas is sufficiently diluted by rare gas.

References

[1] K. Yasutake, H. Ohmi, H. Kakiuchi, T. Wakamiya, and H. Watanabe, Jpn. J. Appl. Phys., 45 (2006) 3592.
[2] T. Suzuki and H. Kodama, Diamond Relat. Mater., 18 (2009) 990.

[3] H. Kodama, A. Shirakura, A. Hotta T. Suzuki, Surf. Coat. Technol., 201 (2006) 913.
[4] H. Kakiuchi, H. Ohmi, K. Nakamura, Y. Yamaguchi, and K. Yasutake, Plasma Chem. Plasma Process., 30 (2010) 579.
[5] H. Kakiuchi, H. Ohmi, T. Yamada, K. Yokoyama, K. Okamura, and K. Yasutake, Plasma Chem. Plasma Process., 32 (2012) 533.
[6] B. Eliasson, M. Hirth, and U. Kogelschatz, J. Phys. D: Appl. Phys., 20 (1987) 1421.
[7] F. Massines, A. Rabehi, P. Decomps, R. B. Gadri, P. Segur, and C. Mayoux, J.Appl. Phys. 83 (1998) 2950.
[8] O. Sakai and K. Tachibana, J. Phys.: Conference Series 86 (2007) 012015.
[9] H. Kobayashi, T. Tandou, H. Nagaishi, K. Suzuki, and N. Negishi, Jpn. J. Appl. Phys., 51 (2012) 08HC04.
[10] S. Sato, H. Yamamoto, Y. Shirouchi, T. Iemori, N. Nakayama, and I. Morita, IEEE Trans. Electron Devices, 23 (1976) 328.
[11] T. Shinoda, M. Wakitani, T. Nanto, N. Awaji, and S. Kanagu, IEEE Trans. Electron Devices, 47 (2000) 77.
[12] K. Suzuki, N. Uemura, S. Ho, and M. Shiiki, AIP Conf. Proc., 636 (2002) 75.
[13] T. Oda, T. Takahashi, H. Nakano, and S. Masuda, IEEE. Trans. Industry Applications, 29 (1993) 787.
[14] H. Yabuta, H. Miyahara, M. Watanabe, E. Hotta, and A. Okino, J. Anal. At. Spectrom., 17 (2002) 1090.
[15] K. Yamakawa, M. Hori, T. Goto, S. Den, T. Katagiri, and H. Kano, J. Appl. Phys., 98 (2005) 043311.
[16] O. V. Penkov, H. J. Lee, V. Y. Plaksin, R. Mansur, and J. H. Kim, Thin Solid Films, 518 (2010) 6160.